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Options for Controlling Condensation Aerosols to Meet Opacity Standards

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16. ABSTRACT: The article gives results of an analysis of the condensing aerosol problem and an evaluation of possible control approaches to reduce the downwind 'detached plume' opacity. (NOTE: The opacity of detached plumes formed by condensation of vapors depends on both the concentration of condensible vapors and the in-stack concentration of fine, submicron, particulate matter.) The opacity of such plumes may be reduced by reducing the concentration of condensible vapors, the in-stack concentration of fine particles, or both. Results of the analysis indicate that, for low concentrations of condensible vapors, the detached plume opacity may be adequately controlled by reducing the in-stack fine particulate concentration alone. For high concentrations of condensible vapors, however, reduction of in-stack fine particulate concentration alone may not be effective: reduction of vapor concentration may be necessary along with particulate removal for adequate reduction of plume opacity. Different combinations of levels of reduction of vapor concentration and particulate phase concentration are possible to achieve a desired result; and thus may be optimized to obtain a cost effective combination.

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Options for Controlling Condensation Aerosols to Meet Opacity Standards

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The opacity of "detached plumes" formed by condensation of vapors depends upon both the concentration of condensible vapors and the in-stack concentration of fine, submicron, particulate matter. This paper provides an analysis of the condensing aerosol problem and an evaluation of possible control approaches to reduce the downwind detached plume opacity. The opacity of such plumes may be reduced by reducing the concentration of condensible vapors or the in-stack concentration of fine particles or both. The results of the analysis indicate that for low concentrations of condensible vapors the detached plume opacity may be adequately controlled by reducing the in-stack fine particulate concentration alone. For high concentrations of condensible vapors, however, reduction of in-stack fine particulate concentration alone may not be effective, and reduction of vapor concentration may be necessary along with particulate removal for adequate reduction of plume opacity. Different combinations of levels of reduction of vapor concentration and particulate phase concentration are possible to achieve a desired result; and thus may be optimized to obtain a cost-effective combination.

In a smoke plume resulting from a combustion process, the opacity may increase in the region of the plume where hot stack gas is mixed with the cooler ambient atmosphere. The phenomenon is often called a "detached plume" because the plume is not continuous at the point of emission. In a broad sense, the plume exhibits a sustained increase in downwind opacity as it is mixed with ambient air. In such a case, an in-stack transmissometer usually will record a lower value of opacity than that obtained by a certified smoke inspector reading the downwind plume opacity.

Interest in a detached plume is often aroused because of regulatory issues. The fact that the opacity of such a plume at the stack is lower than the downwind opacity indicates that the particulate phase at the stack has lower optical obscuration than the downwind plume. The downwind plume opacity thus cannot be related to the particulate mass concentration and size distribution at the stack in a simple manner. Often the particulate mass concentration at the stack as measured by conventional stack tests is well within compliance limits, but the downwind plume opacity is in violation of opacity regulations.

The sustained increase in plume opacity is due to formation of additional optically effective material within the plume. Condensation of vapors such as sulfuric acid vapors, as the plume is cooled by ambient air, is the dominant reason in most cases. Generally, the opacity of a detached plume increases fairly quickly, within 1–2 seconds, after the plume is released from the stack. This indicates that the condensing vapors are probably already present in the stack gases rather than being formed by any secondary reaction mechanisms.

The problem posed by such primary condensible vapors has only recently been recognized, and a systematic strategy or technology to control the visible emissions resulting from materials condensing downwind in the plume has not yet been developed. This paper provides a better understanding of the condensing aerosol problem and an evaluation of possible control approaches to reduce downwind detached plume opacities.

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Literature Survey

Most related information on detached plumes either is unpublished or has not been developed in a systematic manner. Conner[1] reported a significant difference between in-stack opacity at a utility boiler firing high sulfur oil and plume opacity measured downwind with a plume LIDAR (light detection and ranging technique). Opacities over 50 percent were observed in the plume which were believed to be due to condensed sulfuric acid. Probably, the first reported observations of the detached plume opacity, directly relating it to the measured sulfuric acid vapor concentrations, were by Nader and Conner[2] and were presented at a workshop on primary sulfate emission from combustion sources. A number of cases, where the in-stack particulate matter is in compliance with the established standards, yet the downwind opacity exceeds the opacity standard, are currently under negotiations between EPA and industrial and utility companies.

A number of studies have been made to determine the amount of sulfuric acid vapor present in power plant stack gases and to relate it to process operating conditions such as percent excess air used, percent of sulfur in fuel, concentration of SO_2 in the combustion gases, and presence of vanadium which acts as a catalyst for SO_3 formation from SO_2 (e.g., Homolya and Cheney,[3] Hunter and Engle,[4] and Dietz *et al.*[5] Some of the studies have focused on combustion modifications to reduce the amount of acid vapors present (Levy *et al.*[6]). In general, combustion of low sulfur fuel and low excess air/oxygen produce lower sulfuric acid vapor concentrations. The problem of detached plume opacities tends to be more severe for combustors firing oil, which more frequently contains high vanadium content, than those firing coal. Also, oil combustion produces less

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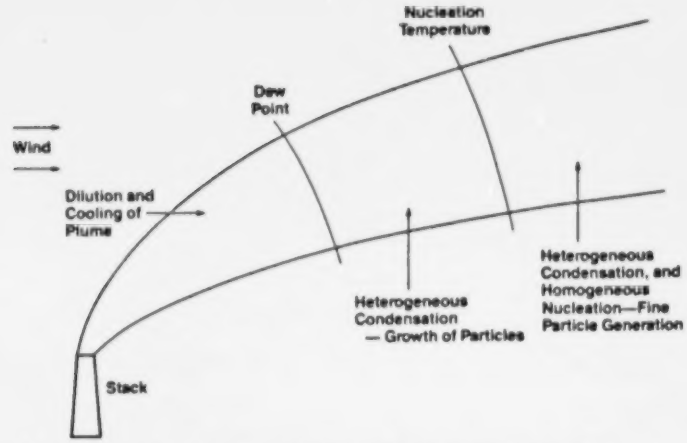

Figure 1. Schematic of condensation and aerosol processes occurring in a plume.

particulate matter (to obscure the effect of vapors) than coal combustion, and the particulate phase is generally high in submicron particle content.

Recently, a mathematical model was developed by Damle *et al.*[7] to quantitatively determine the effect of condensing vapors on the plume opacity. This model includes plume dynamics and the vapor condensation and aerosol processes occurring within the plume as the plume travels downwind. The model indicated a strong influence of both the condensible vapor concentration and the concentration of submicron particulate matter already present at the stack conditions on the peak opacity of the detached plume. These indications were confirmed by another parallel study by Yung *et al.*[8] who experimentally studied sulfuric acid vapor condensation under different process conditions. There are only a few actual field measurements of the "detached plume" opacities, and the measurements often lack detailed information regarding in-stack particle size distribution and concentration, water and sulfuric acid vapor concentrations, and ambient meteorological conditions. However, those measurements and the predictions by the plume model with assumed reasonable values for missing parameters do relate the condensation of vapors to the detached plume opacities.

Scope

A qualitative description of the processes leading to the detached plume phenomenon is first presented followed by a brief description of a mathematical model developed to predict the downwind plume opacities resulting from condensation of existing vapors. Model simulations were carried out to determine the peak plume opacity as a function of sulfuric acid vapor concentration and fine particulate concentration, for a given situation. Possible control approaches of reduction of fine particulate concentration and condensible vapor concentration are discussed next. Recommendations are made to determine a feasible control approach in a given situation. The concentrations of condensible vapor and fine particulate matter in the flue gas at the stack conditions determine the feasibility of a given approach.

Description of Detached Plume Phenomenon

In the case of a "detached plume," the plume usually has very little or no visible emissions at the stack. The opacity may increase suddenly or gradually as the plume travels downwind. Condensation of materials present as vapors at the in-stack conditions is considered to be the dominant cause of the detached plume opacity problem due to the short time after plume release from the stack in which the peak plume opacity appears. The following section briefly describes the condensation and aerosol growth processes occurring in the plume as it travels downwind. This also was the basis of the mathematical model developed by Damle *et al.*[7] The formation and growth of aerosols affect the particulate concentration and size distribution and thus affect the plume opacity.

Plume Dynamics

After emission from a stack, a plume rises due to the initial momentum and buoyancy of the hot plume gas. As the plume rises, it entrains cooler ambient air that cools and dilutes the plume. The rate of entrainment or mixing of the ambient air in the plume primarily depends on plume buoyancy and the velocity differential between the plume and wind. Initially, the dilution rate is, of course, maximum; and it decreases with time as the plume is diluted progressively by the ambient air. The principal parameters affecting the rate of plume dilution and cooling are the plume velocity and temperature, ambient temperature and wind speed, and the atmospheric turbulence and the lapse rate. To predict condensation of vapors and to determine its rate, it is necessary to follow the vapor concentration and temperature variations with time after plume release. By setting up appropriate mass, momentum, energy, and species balance equations across a plume section and following this plume section with time, the change in the plume properties with time is determined.[7]

Vapor Condensation

As the plume cools, the plume temperature may drop below the dew point for the condensible vapors, thus commencing condensation. Figure 1 is a schematic of the condensation and aerosol processes occurring in a plume. Two primary approaches are available for the condensation process—heterogeneous condensation and homogeneous nucleation. The relative contribution of the two mechanisms to the condensation process at a given time depends upon the supersaturation ratio of the condensible species, which is the ratio of the partial pressure of the vapor to its equilibrium vapor pressure at the prevailing conditions.

Heterogeneous condensation. Upon reaching the dew point, vapors may begin to condense heterogeneously on the available surface area of existing particulates in the plume. For low supersaturation ratios (<5), this provides the dominant condensation mechanism. The rate of heterogeneous condensation on a particle is given by the rate of diffusional transport of vapors to the particle surface and depends on the vapor concentration gradient and the diameter of the particle. Relations to determine the rate of heterogeneous condensation and corresponding growth of particles are well developed for particles in both continuum and molecular regime (Friedlander[9]). An approximate relation applicable to the entire particle size range has also been proposed by Fuchs and Sutugin.[10]

Homogeneous nucleation. As the vapors condense heterogeneously, the supersaturation ratio of the condensible species may increase or decrease depending on the rate of heterogeneous condensation of the vapors and the rate of continued cooling and dilution of the plume by ambient air. If sufficient surface area is not available for the hetero-

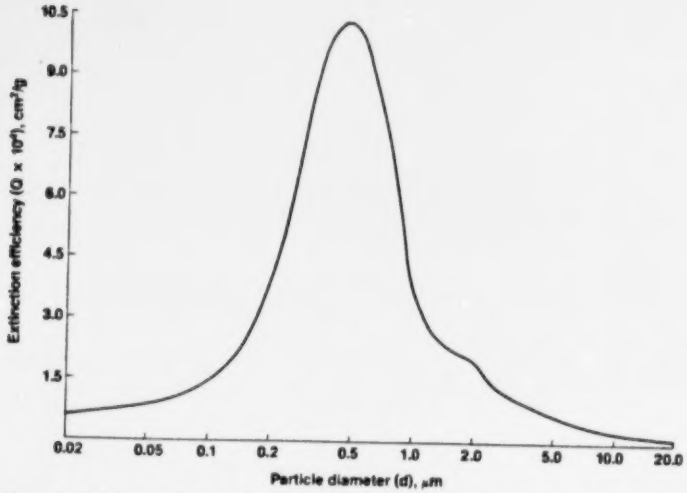

Figure 2. Specific extinction efficiency per unit mass of particles.

geneous condensation process, the supersaturation may increase to a point where the homogeneous nucleation of the vapors becomes appreciable. The temperature at which the nucleation process becomes significant, generating at least 1 droplet/s/cm^3, is termed "nucleation temperature." The homogeneous nucleation process generates many very fine droplets, of a stable critical size, which in turn provide a large surface area for the condensation to proceed by the heterogeneous mechanism. The actual amount of vapor condensed by this mechanism is often very small but it provides a large surface area on which the condensation can proceed heterogeneously. The critical size of the generated droplets depends on the supersaturation ratio and the physical properties of the condensed phase. Classical nucleation theory may be used to determine the stable critical size and the rate of generation of droplets of this critical size.[9]

Growth of Particles and Plume Opacity

Growth of existing particles by heterogeneous condensation and formation of new particles by homogeneous nucleation change the particulate size distribution and concentration in the plume. In addition, interparticle collisions also change the size spectrum of particles, although this is significant only for very fine particles. The change in the concentration and size distribution of the particulate phase in the plume determines the change in the plume opacity. The opacity of a plume may be determined by[11]:

$$O_p = 100[1 - \exp(-2Rb_{ext})] \quad (1)$$

where O_p is the percent plume opacity, R is effective plume radius, and b_{ext} (cm^{-1}) is overall extinction coefficient of the particles, and is given by:

$$b_{ext} = \pi/6 \int_{d_{min}}^{d_{max}} Q_i d_i^3 n_i dd_i \quad (2)$$

where Q_i is specific extinction efficiency per unit mass for a particle of size d_i, and n_i is the number concentration of particles of size d_i.

The increase in the plume opacity is due to formation of additional optically effective material within the plume. The particles in the 0.2–1.0 μm diameter range are particularly effectve in obscuring visible light on a unit mass basis, with a peak obscuration at 0.5 μm particle diameter. Figure 2 shows scattering efficiency per gram, Q, as a function of particle diameter for a particle refractive index of 1.5–0.05i and a light wavelength of 550 nm. The ultrafine particles (less than 0.1 μm diameter) are actually less effective than the above size range, but have a potential to grow into the optically most effective size range by the condensation process. The fine particles also offer a large surface area per unit mass for the condensation process. The submicron particles present in the plume are thus very important in determining the plume opacity for two reasons: 1) particles already in the optically effective size range, and 2) smaller particles which can rapidly grow into that range.

The characteristic particles in the 0.1–0.15 μm size range, typical of the coal fired power plant fly ash size distribution,[12,13] thus play a very important role in determining the plume opacity. The measurements by Markowski *et al.*[14] indicated the presence of such a submicron mode at both the inlet and outlet of a high efficiency ESP following a pulverized-coal-fired utility boiler. Measurements at six coal fired boilers by McElroy *et al.*[15] also identified such distribution. Submicron particles are even more significant for oil fired combustors: they can constitute almost half of the total particulate emissions, as indicated by measurements of Mormile *et al.*[16] The submicron particles appear to be a general feature of coal or oil combustion and are produced by a vaporization/condensation mechanism. Referring to Figure 2, there is almost tenfold variation in the extinction efficiency, Q for particles in the narrow range of 0.1–1.0 μm diameter. Therefore, the mass distribution of the particles within this range has significant effect on the plume opacity. It is, however, difficult to measure the submicron particles concentration and size distribution in the flue gas emissions, and the resolution of available techniques is also limited for the submicron range.

In the absence of any fine particles in the plume, the homogeneous nucleation process becomes important and generates many ultrafine particles which may eventually grow by condensation and coagulation into the optically effective size range. In such a case, the rate of growth of the ultrafine par-

Table I. Base case parameters.

Initial plume parameters (at stack exit)	
Diameter	4 m
Gas temperature	200°C
Velocity	20 m/s
Inclination	90° (vertical)
Water vapor concentration	5% by volume
Sulfuric acid vapor concentration	10 ppm
Large particle concentration	100 mg/m^3
Number mean diameter	4 μm
Geometric standard deviation	1.8
Fine particle concentration	10 mg/m^3
Number mean diameter	0.15 μm
Geometric standard deviation	1.3
Molecular weight of gases	29
Ambient parameters	
Wind speed	5 m/s
Temperature	20°C
Relative humidity	50%
Sulfuric acid concentration	0
Particulate concentration	0

Table II. Effect of parameters on peak plume opacity (simulation study).

No.	Case	Initial opacity %	Peak opacity %
1	Base	11.1	38.1
2	Low sulfuric acid vapor concentration (3 ppm)	11.1	18.8
3	High sulfuric acid vapor concentration (30 ppm)	11.1	73.9
4	Low fine particle concentration (1 mg/m^3)	5.1	13.8
5	High fine particle concentration (100 mg/m^3)	53.8	68.8
6	Low large particle concentration (10 mg/m^3)	7.4	35.7
7	Low water vapor concentration (1%)	11.1	37.5
8	High water vapor concentration (20%)	11.1	34.3
9	Low initial plume temperature (125°C)	11.1	39.2
10	Low wind speed (1 m/s)	11.1	41.8
11	High wind speed (20 m/s)	11.1	19.3
12	Low ambient relative humidity (5%)	11.1	38.2
13	High ambient relative humidity (95%)	11.1	37.2
14	Low ambient temperature (1°C)	11.1	35.0

ticles with respect to plume dilution becomes important in determining the plume opacity. For high vapor concentrations, the growth rate may become high enough for the particles to grow into the optically effective size range, thereby dramatically increasing the plume opacity.

Parameters Controlling the Condensation Process

The condensation process as described above depends on a number of parameters that determine the condensation mechansim and the rate of the condensation. The primary variables are the condensible vapor concentration and the concentration and size distribution of the particulate phase, especially of the submicron fraction present in the plume. Parameters affecting the entrainment or dilution rate of the plume are also important: they determine the change in the plume velocity, temperature, and vapor and particulate concentrations with the plume's travel downwind. These parameters include plume velocity, ambient wind speed, plume buoyancy with respect to ambient air, and atmospheric lapse rate. The rate of plume dilution and cooling determines the time available for the heterogeneous condensation process before the homogeneous nucleation becomes significant. The effect of these various parameters on the plume opacity is discussed in the following sections.

Plume Opacity Prediction

Plume Model

To determine the opacity of a plume as a function of plume travel, the particle size distributions and concentrations need to be obtained, along with the effective plume radius, as a function of time elapsed after plume release from a stack. The mathematical model developed by Damle *et al.*[7] is dynamic in nature and follows a plume as it travels downwind. The conservation equations of mass, momentum, energy, and species mass are solved to determine the plume properties such as velocity, effective radius, temperature, and species concentration as a function of time or the distance traveled from the stack. By using the gas-phase vapor species concentration, a dew point is determined. If the gas-phase temperature is lower than the dew point, the rate of vapor condensation, growth of existing particles, and the rate of formation of new particles are determined by appropriate equations for both condensation mechanisms. Using the updated particulate concentration and size distributions, plume opacity is determined as a function of time.

The computer program "PLUME" was written in FORTRAN to solve all the pertinent equations and simulate a plume. The details of the program are reported elsewhere.[7,17] Plume simulations were carried out using this program to determine the effect of various parameters on the plume opacity as discussed below.

Model Simulations

The most frequently encountered condensible material in detached plumes is sulfuric acid. Sulfuric acid is also very hygroscopic, and its equilibrium properties are strongly related to the water vapor content of a plume. Therefore, binary condensation of sulfuric acid and water is considered in the model simulations described here. Power plant fly ash emissions from both coal and oil fired boilers typically exhibit a bimodal particle size distribution, with fine particle peaks of about 0.15 μm diameter. The mean size of the large particles is difficult to determine, especially for the uncontrolled emissions, since the first stage in the cascade impactor usually collects particles larger than 10 μm. For controlled sources, the large particles may be 4–6 μm in mean diameter. For the simulations presented here a bimodal lognormal size distribution was used: the mean size of fine particles was 0.15 μm diameter, and that of large particles was 4 μm. The proportions of the respective modes depend on the type of fuel used and the efficiency of the particulate control equipment. For the base case simulation, a 10:1 ratio was used with a large particle concentration of 100 mg/m^3 and that of fine particles of 10 mg/m^3.

To assess the effect of various parameters identified in the previous section, several plume simulations were carried out. A base case was first established by using typical ambient and stack gas conditions. A sulfuric acid concentration of 10 ppm and water vapor content of 5 percent by volume in the flue gas were used in the base case. A single component was then varied with respect to the common base case to determine the effect of that variable. The base case parameters given in Table I were used in these simulations.

The results of these simulations are shown in Table II which shows that the most influential parameters are the in-stack concentrations of both sulfuric acid vapor and fine particles. The ambient parameters wind speed and the corresponding entrainment rate do have a moderate influence on the plume opacity; however, they are not controllable parameters, and obviously cannot be considered in the control approaches.

To further illustrate the effect of in-stack concentrations of sulfuric acid vapor and the fine particle fraction of total particulates, additional simulations were carried out: the fine particle

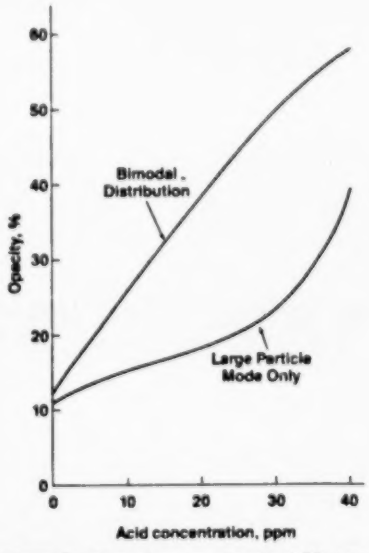

Figure 3. Peak plume opacity with H_2SO_4 concentration.

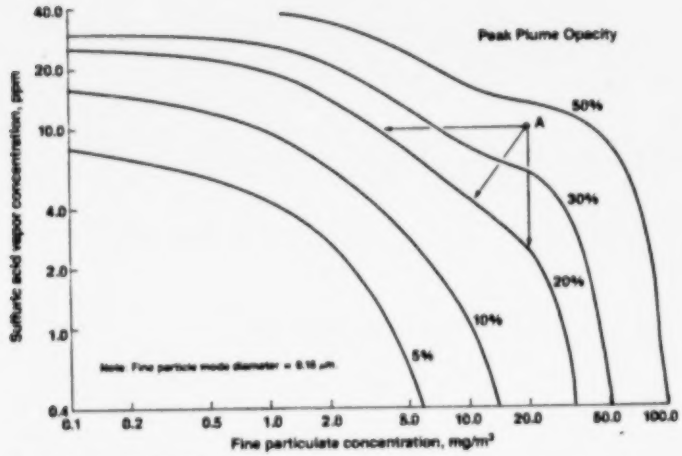

Figure 4. Iso-opacity plot.

concentration was reduced to 2 mg/m³ (about 2 percent of total particulate mass), and the mean size for the large particle mode was lowered to 2 μm. The results are shown graphically in Figure 3. In spite of the lower concentration of the fine particulate fraction, its presence has substantial effect on the plume opacity as seen by the difference between the peak opacity with the bimodal distribution and that with only the large particle fraction. The reasons for the effectiveness of the fine particle mode have already been discussed. Note that the mean size of the submicron fraction is also important in determining the plume opacity and that somewhat different results will be obtained by changing the mean size and concentration of the submicron size fraction.

Because of the dominant effect of the condensible vapor concentration and the concentration and mean size of the submicron particulate fraction, any control approaches for the reduction of the detached plume opacities must be based on them. The plume opacity may be reduced by reducing either or both of these concentrations. Different combinations of the concentration levels for both the vapor phase and fine particulate phase may thus be possible to achieve a desired result.

Possible Control Approaches

As mentioned earlier, both the concentration of the condensible vapor and that of the fine particle fraction of the fly ash present in the stack gases have a strong influence on the detached plume opacity. Consequently, to achieve a desired peak plume opacity different combinations of these two variables may be selected. A number of simulations were, therefore, carried out to obtain the iso-opacity lines as a function of the acid vapor concentration and the fine particle mode concentration for one set of parameters. The large particle mode primarily has an additive effect in determining the overall extinction coefficient of the plume. Therefore, these simulations were carried out by setting the large particle concentration equal to zero. All other variable values were those used in the base case simulation described earlier. The results are shown graphically in Figure 4, for small particles at 0.15 μm number mean diameter. Incidentally, a small change in this mean mode diameter can also have some small effect on the plume opacity, as seen in Figure 5, obtained with a mean diameter of 0.1 μm. The opacities indicated in Figure 4 do not include the contribution by the large particles, which may be easily done by considering the in-stack opacity for the total particulate phase. Also, note that other parameters (e.g., water vapor concentration, plume velocity, and ambient conditions) do affect plume opacity, although moderately. The fine particle size distribution is assumed to be lognormal with a geometric standard deviation of 1.3, whereas the actual distribution may be different. Thus, Figure 4 is not unique; it needs to be reconstructed for any specific case.

In Figure 4, a given situation in a certain detached plume opacity problem is indicated as a point (e.g., point A in Figure 4 represents 10 ppm of sulfuric acid vapor and 20 mg/m³ of fine particulate phase in the stack gas). The desired opacity is, however, shown by a line of different vapor and fine particulate concentration combinations (for example, the iso-opacity line of 20 percent opacity in Figure 4). Several approaches are thus possible to achieve a desired opacity; e.g., by reducing vapor concentration, or by reducing fine particulate concentration, or by both (as shown by arrows from Point A in Figure 4). Reduction in fine particulate concentration does not normally affect the vapor concentration. The condensible vapors may be reduced either in the gas phase (by using a dry reagent to remove vapors or by processs modifications) or in the liquid phase (by condensation followed by droplet collection along with other particulate matter). The liquid phase removal of condensible vapors directly affects the particulate concentration as the condensation process generates additional droplets. The gas-phase removal of vapors is also likely to increase, although indirectly, the particulate concentrations. These possible approaches are shown schematically in Figure 6. The iso-opacity lines for a given case identify the concentration reductions required in a given approach. The individual approaches of reducing fine particulate concentration or vapor concentration are considered below for their applicability, advantages, and disadvantages.

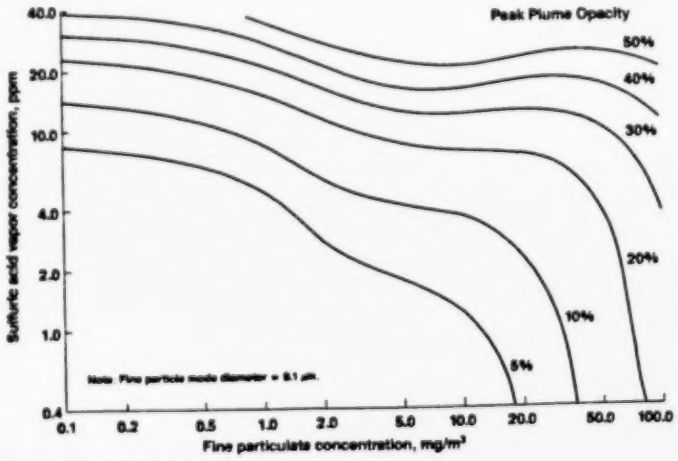

Figure 5. Iso-opacity plot.

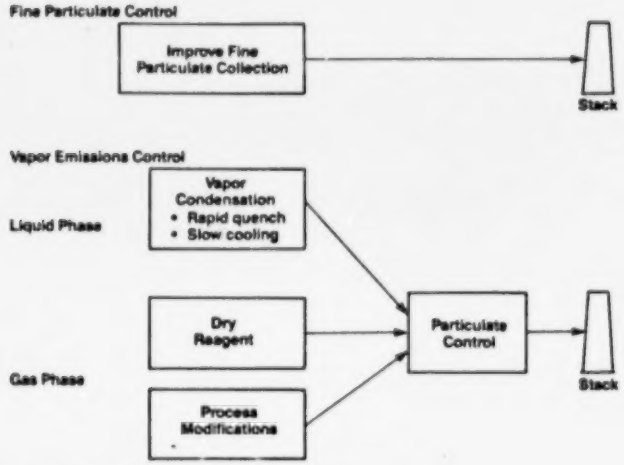

Figure 6. Schematic of possible control approaches.

Control of Fine Particle Concentration

The approach of reducing existing fine particulate concentration, if feasible, is probably the simplest. Its feasibility, however, depends not only on the particulate phase concentration and efficiency of the existing particulate collection system, but also on the level of sulfuric acid vapor present. For low vapor concentrations, the opacity may be reduced satisfactorily by a moderate reduction in the fine particulate concentration; but, at a high vapor concentration, even a large reduction in fine particulate concentration may not achieve the desired plume opacity level.

For example, referring to Figure 4, for a 10 ppm acid vapor concentration, a factor of 2 reduction (from 7 to 3.5 mg/m^3) in fine particulate concentration will reduce the opacity from 30 to 20 percent and may be satisfactory. However, the same reduction in fine particulate concentration for an acid vapor concentration of 20 ppm will reduce the opacity from 50 to 35 percent and will not be satisfactory. At a 20 ppm acid vapor concentration, further reduction of fine particulate concentration from 3.5 to 1.0 mg/m^3 will be required for the desired 20 percent opacity.

If the existing particulate control facility can achieve the required reduction in fine particulate concentration, either by improving the performance and capacity of an existing unit or by upgrading the facility, such an approach of reducing fine particulate concentration to reduce the plume opacity will be feasible. The main advantages of this approach, if feasible, are the simplicity of the approach, retrofit possibilities to an existing facility, and that the particulate concentration will be reduced without affecting the acid vapor concentration. The applicability of this approach, of course, depends on the capability of the existing particulate control facility and any possibility of upgrading it if required. By noting the typical fine particulate concentrations at the outlet of high performance particulate control equipment, such as an ESP or a baghouse, tolerable concentrations of acid vapor in the flue gas can be estimated for a certain maximum plume opacity; e.g., 20 percent.

In a performance evaluation program carried out by Gooch and Merchant,[18] the performance of six ESPs was evaluated. Based on their measurements, average emissions of total particulate matter at the ESP outlets under normal operation were about 16.5 mg/m^3; and average emissions of fine particulates were about 3.0 mg/m^3. In the same study, fine particulate emissions less than 1.0 mg/m^3 were also often noted in some tests. Referring to Figure 4, an average outlet concentration of fine particulates of 3.0 mg/m^3 will allow sulfuric acid vapor emissions of about 8 ppm for a maximum opacity limit of 20 percent, assuming a 4 to 5 percent opacity contribution by the large particle mode. If a particular facility can limit the fine particulate emissions below 1.0 mg/m^3, it can allow as much as 20 ppm of sulfuric acid vapor in the flue gas emissions for a maximum opacity limit of 20 percent. Note that, based on Figure 4, any further reduction in fine particulate emissions will not allow any significantly higher sulfuric acid vapor emissions in the flue gases. Baghouses typically have lower particulate matter emissions than ESPs. Based on a performance evaluation of a fabric filter by Ensor *et al.*,[19] total particulate emissions are typically less than 5.0 mg/m^3. The fine particulate emissions may, therefore, be expected to be less than 1.0 mg/m^3. Therefore, based on Figure 4, baghouses may typically allow as much as 20 ppm of sulfuric acid vapor in flue gas emissions, for a maximum opacity limit of 20 percent.

If, in a given situation, the sulfuric acid vapor emissions are such that any possible and reasonable reduction in fine particulate concentration is not adequate to lower the plume opacity to a desired level, sulfuric acid vapor concentration need to be reduced to achieve the desired opacity level. In such a case, reduction of fine particulate concentration alone will not be technically feasible.

Reducing Acid Vapor Concentration

For high sulfuric acid vapor concentrations in the flue gas, it will be necessary to reduce the acid vapor content to meet the opacity requirements. For example, as indicated by the discussion in the previous section referring to Figure 4, if the vapor level exceeds 20 ppm in the flue gas, vapor removal will most likely be required to meet a 20 percent plume opacity requirement. The vapor concentrations may be reduced in the liquid phase or in the gas phase. In the liquid-phase removal, vapors are first condensed. Based on the rate of gas cooling, the condensation process may be divided in two groups: rapid quenching of the gas phase by direct contact with water, and slow cooling of the gas as in a heat exchanger/condenser. The vapors may be removed in the gas phase by using a reagent that selectively reacts with the vapor species. It may also be possible to reduce the gas-phase vapor concentrations by modifications of processes responsible for vapor generation. Thus, the possible approaches for reduction in the vapor concentration are:

1) Rapid quenching of the flue gas in a water/flue gas contactor—a packed bed, for example.
2) Slow cooling of the flue gas in a heat exchanger.
3) Injection of a dry active reagent such as nacholite.
4) Process modifications to reduce generation of acid vapors.

One principal difference in approaches for vapor removal, as compared to those for particulate removal, is that all above-mentioned vapor removal processes are likely to produce additional particulate loadings in the flue gas; whereas, reducing the fine particulate concentration is not likely to affect the acid vapor concentration. Approaches (1) and (2) condense the vapors, directly converting them into particulate matter. In Approach (3), fine reagent powder is injected into the flue gas to form the additional particulate loading. Approach (4), if based on

using less excess air/oxygen in the combustion process, may produce incomplete combustion, thereby increasing the particulate loading. Therefore, any consideration of these approaches must also include adequate removal of the additional generated particulate matter. Since the submicron particles are the hardest to collect in a particulate control device, attempts must be made to minimize the fine particulate concentration during vapor removal, especially by condensation.

An experimental program was recently undertaken by Yung *et al.*[8] to study the condensation of sulfuric acid vapors. In this program, vapor condensation was studied under different operating conditions using three process configurations: rapid quenching, dilution cooling, and slow cooling. In all experiments, the size distribution and concentration of the aerosols generated by the condensation process and the amount of the acid vapor condensed were measured as a function of different operating parameters. These results, especially for the rapid quenching and slow cooling experiments, indicate the operating conditions which minimize the fine particulate formation in these condensation processes.

These four approaches are considered separately for their feasibility and applicability.

Rapid quenching of the flue gas. This process inherently generates a large number of sulfuric acid vapor droplets by homogeneous nucleation, and attention must be given to minimize submicron particulate formation. In this approach, the flue gas may be directly contacted by quench water in a packed bed or spray column. In the experiments by Yung *et al.*[8] simulated flue gas containing known amounts of sulfuric acid vapor, water vapor, fly ash, and SO_2 was quenched in a randomly packed bed of berl saddles by a known countercurrent flow of quenching water. These experiments indicate that higher acid vapor concentration, lower quench water temperature, and higher water vapor concentration reduce the proportion of fines in the total particulates. Their experiments also show that almost all of the acid vapors can be condensed in this process, and that about 50 percent of the total amount of acid is condensed in the bed. The fly ash, although somewhat effective in scavenging the acid droplets, did not prevent the acid vapor from nucleating into fine droplets.

Condensation of 1 ppm of acid at 120°C generates about 3.5 to 4 mg/m^3 of particulates. Thus, based on the amount of sulfuric acid vapors in the flue gas and the measured size distribution of the generated aerosols in the above mentioned experiments, the amount of total and fine particulates generated in this process may be estimated. This information may then be used to determine the additional particulate loadings and the adequacy of the existing particulate control equipment to handle them. Since this process removes almost all of the acid vapors, the in-stack particulate loading is measurable by standard stack sampling techniques (e.g., Method 5), and the correlation between the in-stack particulate mass and the opacity is restored.

This process is suitable for high acid vapor concentrations as indicated by experiments. This is not actually a limitation, since such vapor removal will most likely be undertaken for high acid vapor concentrations anyway. This process also favors high flue gas moisture content which allows growth of the condensed droplets in the scrubber. It may be worthwhile even to consider injecting waste steam, if available, into the flue gas to increase the water vapor concentration. This essentially is the Flux/Force Condensation System suggested by Calvert *et al.*[20] to remove fine particulates. Since this process removes almost all of the acid, based on Figure 4, up to 30 mg/m^3 of fine particulate may be allowed in the emissions without violating the 20 percent opacity limit. This fact may allow an existing particulate control facility to handle the additional particulate loading. Additional factors that must be considered in evaluating the feasibility of this process are: additional space and ducting required for the scrubber equipment, the material of construction for the scrubber to handle the condensed dilute acid, the possibility of corrosion in subsequent particulate control equipment due to collection of acid droplets, the additional pressure drop across the scrubber, and the need for reheating the flue gas before stack exit.

The ability of the existing particulate control equipment to handle the greater particulate loading at lower temperature, especially additional acid droplet loading, is very important as it can have direct impact on the economics. If the existing equipment is not suited for acid droplets and/or lower temperature, it may be necessary to install the quench scrubber following the existing primary particulate control system. Additional smaller size particulate control equipment capable of handling acid droplets will then be needed to remove generated acid droplets.

Slow cooling. This process relies on controlled cooling so that the gas temperature is lowered below the dew point (to commence condensation), but held above the nucleation temperature (to prevent any homogeneous nucleation from generating fine droplets). This method is better suited for lower acid vapor and water vapor concentrations, as this allows a better control on the cooling and condensation process. The presence of fly ash is very important in this process, as it allows a large surface area on which the vapors can condense. In the experiments by Yung *et al.*,[8] higher acid vapor concentrations resulted in large numbers of fine particulates by nucleation. Thus, for high acid vapor concentrations, applicability of this process over rapid quenching is questionable. Also, this will be a very difficult system to design because close control of gas cooling and temperature is required. One advantage of this process is that, if successful, large amounts of acid will condense on existing fly ash particulates and condenser walls, thus generating only a small amount of additional fine and total particulate loading.

For low acid vapor concentration, this process may be preferable to rapid quenching; however, in such a case, plume opacity may be controlled adequately by reduction in fine particulate concentration alone. For low vapor concentration, reducing fine particulate matter is better suited than slow cooling due to process simplicity and the possibility of retrofit applications. As for rapid quenching, attention must also be given to other important factors; e.g., additional space and equipment, the material of construction, corrosion in the particulate control system, additional pressure drop, and the need for reheat. The ability of the existing particulate control system to handle acid droplets must also be considered.

Injection of Dry Reagent. One advantage of this approach is that it does not generate additional fine particulate matter. The dry powder used is usually coarser, with a mean diameter of 20 to 100 μm. Thus, although this process will generate additional particulate loading, it will not be difficult to collect. Nacholite has been successfully used to remove SO_2 from flue gas with moderate efficiency, and the sulfuric acid may be expected to be even more reactive than SO_2. Such dry injection processes for SO_2 have typically been used with a baghouse, and the cake deposit on the fabric bags containing the reagent is thought to provide the necessary gas-phase/reagent contact. Thus, such a process may be better suited in conjunction with existing baghouse facilities. Spray drying has also been used to remove SO_2; however, such a process leads to quenching of the gas phase which in this case will produce many fine droplets which will not be scavenged by the reagent slurry droplets.

In evaluating this process, the ability of the reagent (e.g., nacholite) to react with a relatively low concentration of acid vapor must be determined. The concentration of SO_2 to which this process has been applied is usually of the order of 500 ppm. Whether such reactivity will be observed with 50 ppm or less of sulfuric acid vapor must be determined experimentally. No such data are known to be available. If the dry reagent is found to be reactive enough to remove small quantities of sulfuric acid vapor efficiently, this process will be a good alternative to the above mentioned condensation processes.

Process modifications. This control approach is aimed at reducing the amount of sulfuric acid vapor generated in the fuel combustion process, rather than removing the generated acid vapors. Several studies have evaluated the effect of different operating conditions on the sulfuric acid vapor emissions: they indicate that the percent of sulfur in fuel and the percent of excess air/oxygen used in the combustion process predominantly determine the acid vapor emissions. Additionally, oil fired units are generally found to produce greater emissions of the acid vapor as compared to coal fired units. This difference is generally attributed to the presence of vanadium in the fuel oil which serves as a catalyst in the SO_2 conversion reaction.

Fuel combustion produces almost quantitative amounts of SO_2. The conversion of SO_2 to SO_3 and primary sulfates is predominantly a function of excess oxygen levels in the combustion gases and the presence of catalysts such as vanadium. Thus, for a given combustion facility almost quantitative reduction in SO_2 and SO_3 emissions can be achieved by reducing the sulfur content of the fuel. The use of low sulfur fuel, as a control option, is limited, however, by the cost and availability of such low sulfur fuel. Note that this control option is mandatory in some parts of the United States, e.g., New York City.

Emissions of SO_3 from utility and industrial boilers typically vary from 1 to 6 percent of total SO_x depending on percent excess air/oxygen. The available data in the literature, however, show much scatter.[3,4] Theoretical computation by Hunter and Engel[4] indicated about 3 percent conversion at 2 percent excess oxygen with a leveling in the percent conversion at higher oxygen levels. At levels of oxygen less than 2 percent, almost linear variation of flue gas SO_3 concentration has been observed with respect to excess oxygen (e.g., Dietz *et al.*[5]). Thus, based on theoretical calculations and field measurements, it appears to be possible to reduce SO_3 emissions by reducing excess air used in the combustion process. Successful operation of a combustor with low excess air requires that the oxygen in the flue gas be maintained at levels below 0.2 percent. Attention must be given in such operation to possible additional particulate phase formation due to incomplete combustion. Such operation requires precise control of the fuel/air ratio in all parts of the combustion system. Such a low excess air operation is more practical for oil-fired systems; the required technology is not available for coal-fired systems (Levy *et al.*[6]).

Levy *et al.*[6] also investigated effects of other combustion modifications (e.g., staged combustion and flue gas recirculation) on SO_3 formation. In staged combustion, even an enhancement of SO_3 formation was found to be possible; whereas, other combustion modifications were found to have little or no effect on the SO_3 concentration in the flue gas. Thus, besides using a low sulfur fuel, operation at low excess air appears to be the only process modification capable of reducing the amount of SO_3 generated. This approach is also probably suited only for oil-fired units.

Conclusions and Recommendations

The problem of "detached plume" opacity caused by condensation of sulfuric acid vapors was analyzed using basic principles involved in this physical process. The concentration of condensible vapors and the concentration of fine particulate matter in the flue gas are the most important parameters influencing the maximum downwind plume opacity. Control strategies to reduce the detached plume opacity must, therefore, be based on reducing the fine particulate concentration in the flue gas, or the condensible vapor concentration, or both. Using the "PLUME" model, iso-opacity lines may be constructed as a function of the concentrations of the condensible vapors and those of the fine particulate phase for a given situation, taking into account all other system, operating, and ambient meteorological parameters. The iso-opacity lines provide a graphical indication of possible control approaches.

In general, for low sulfuric acid vapor concentrations, typically below 20 ppm, reduction of fine particulate concentration alone may provide adequate control of the plume opacity. For higher sulfuric acid vapor concentrations, reduction in acid vapor concentration will generally be necessary along with adequate particulate control to reduce the plume opacity. Three specific approaches may be possible in reducing the acid vapor concentration: use of low sulfur fuel, rapid quenching of the flue gas in a packed bed scrubber, and combustion under low excess air conditions. In the latter two approaches, especially in flue gas quenching, attention must be given to additional particulate-phase formation which must be handled by the existing particulate control system. The low excess air operation may be suitable only for oil-fired systems. Injection of dry reagent powder may also be a feasible approach to remove acid vapors in the gas phase, although experimental data are needed to verify it.

In summary, this paper outlines the boundaries of the condensation aerosols problem. Established control technology to reduce the detached plume opacity problem, especially to reduce vapor concentrations in the flue gas, does not exist at this time and must be developed for effective control of plume opacity. Possible approaches in that direction are outlined in this paper.

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